



Electrocatalytic properties of diamond in the oxidation of a persistant pollutant

Elena Guinea ^a, Francesc Centellas ^a, Enric Brillas ^a, Pablo Cañizares ^b, Cristina Sáez ^b, Manuel A. Rodrigo ^{b,*}

^a Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

^b Department of Chemical Engineering, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

ARTICLE INFO

Article history:

Received 13 November 2008

Received in revised form 26 January 2009

Accepted 31 January 2009

Available online 6 February 2009

Keywords:

Diamond

Electrooxidation

Electrocatalytic properties

Wastewater

Persistent

ABSTRACT

This work is focused on the study of the role of several conductive-diamond characteristics (boron doping, sp^3/sp^2 ratio, diamond-layer thickness) on the performance of the electrolysis of enrofloxacin (as model complex-organic pollutant). Commercial lots provided by an important conductive-diamond manufacturing company have been used. Results show that enrofloxacin electrooxidation is strongly influenced by the conductive-diamond characteristics; particularly the ratio diamond/graphite carbon was found one of the most significant parameters in this process: the higher the content in diamond-carbon the greater the TOC and COD decays in the bulk electrolyses. These results have been interpreted in terms of the oxidation mechanism involved. High graphite content favours direct oxidation of the pollutant on the electrode surface and leads to the formation of many intermediates. On contrary, high diamond content seems to favour the complete oxidation of the organic to carbon dioxide, thanks to the contribution of the oxidants (hydroxyl radicals and electrogenerated reagents) present in a region close to the electrode surface. Likewise, the oxidation rate seems to be improved with increase in the concentration of boron and decrease in the thickness of the substrate layer.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

During the last century, significance of a pollutant was understood in terms of quantity, and many types of technologies were especially developed to remove from urban wastewaters the pollutants contained in large concentrations. However, these technologies are not able to diminish completely the presence of some anthropogenic pollutants of complex quality (pharmaceutical degradation products, cleaning reagents, etc.), and these persistent pollutants are being accumulated in the environment after their discharge.

Nowadays, detection in noticeable concentrations of a high number of such compounds in surface and ground drinking waters is common [1–6]. The presence of these emerging pollutants in the aquatic environment presupposes a potential risk as they can affect, among many other aspects, the endocrine system of fishes and, even, they can exert toxic effects on algae [7].

The removal of these persistent organics is difficult and, presently, only chemical and advanced oxidation technologies are

reported to obtain satisfactory results [8]. In recent studies [9,10], it is pointed the electrochemical techniques as a good alternative for the removal of these persistent pollutants. In fact, with the development of new materials, like the diamond boron doped (BDD) electrodes, electrochemical advanced oxidation processes (EAOPs) have been revealed as the more efficient and environmentally compatible technique for the removal of a great variety of organics [11–22]. Results show that EAOPs allows achieving good efficiencies during no excessively-long mineralization processes, with an easy methodology and no significant degradation products. Unfortunately, most of these studies have been focused on the study of the feasibility of the use of this technology to treat different types of pollutants and on the selection of the experimental conditions to improve the performance of this technique. However, the effects of the characteristic of the conductive-diamond electrodes in the bulk electrolyses results have not been discussed in detail, although it seems reasonable to think that the electrochemical process can be greatly influenced by the nature of the diamond electrode used. The information about how diamond characteristics affect to the electrochemical processes can help to explain some experimental results. Recent works [23,24] show that the conductive layer characteristics (sp^3/sp^2 ratio, boron content, the thickness of the BDD layer) and the

* Corresponding author. Tel.: +34 9902204100x3411; fax: +34 926295256.

E-mail address: Manuel.Rodrigo@uclm.es (M.A. Rodrigo).

substrate properties (resistivity and roughness of the surface) have an important influence on electrolysis of phenol and phosphate solutions. Results show that phenol oxidation is strongly influenced particularly by the roughness of the surface: the rougher the surface, the better the efficiencies obtained. In addition, and contrary to what it can be expected, the thickness of the diamond layer seems to be the most significant parameter in the electrosynthesis of peroxophosphate: the thinner the layer, the better the results obtained. Likewise, in this former process, the boron content increases the efficiency but this effect is only observed for very high boron contents. The interactions between the electroactive species and the diamond surface seem to be very important in order to explain the electrolytic results, and even to elucidate the oxidation mechanisms involved in the conductive diamond electrochemical oxidation (CDEO), and even to clarify the electrocatalytic properties of high-oxygen overvoltage anodes in the oxidation of organics, as it was previously discussed in literature [25–30].

With this background, the goal of this work has been to study the influence of the main characteristics of the diamond electrodes on the mineralization efficiency of a model pharmaceutical pollutant: enrofloxacin. This compound is present in wastewaters and natural waters in concentrations up to $0.6 \mu\text{g dm}^{-3}$ [1–7]. It has been found that these compounds can be removed up to 85% during treatment in sewage treatment plants; although they are mainly accumulated in the sewage sludge where persist after anaerobic digestion [3,31]. Thus, the complexity and persistent properties of this molecule makes interesting the study of the electrochemical removal of this compound and also the study of the influence of the diamond properties in the removal efficiency. To do this, it has been used sample-electrodes provided by one of the more important diamond-electrodes manufacturers (Adamant Technologies, Switzerland), specialist in the manufacture of conductive-diamond layers on p-Si substrates. Results obtained will help to elucidate the effect of the electrocatalytic properties of diamond in the oxidation of a model persistent pollutant.

2. Experimental

2.1. Chemicals

Enrofloxacin was analytical grade (>99% purity) supplied by Laboratorios Carlier S.A. (Barcelona, Spain). Anhydrous sodium sulphate used as supporting electrolyte was analytical grade purchased from Fluka. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system, with resistivity >18 MΩ cm at 25 °C. Sulphuric acid and sodium hydroxide utilized to adjust the solution pH were analytical grade supplied by Merck.

2.2. Analytical procedures

The organic load of the initial and electrolyzed solutions was monitored by their chemical oxygen demand (COD), determined with a HACH DR/2000 analyzer. The removal of total organic carbon (TOC) of the same solutions was determined with a Shimadzu TOC-5050 analyzer. The solution pH was measured with an InoLab WTW pH-meter.

2.3. Electrochemical cells

All electrochemical measurements were made with an Eco-chemie Autolab PGSTAT 30 potentiostat/galvanostat. CDEO trials of enrofloxacin synthetic wastes were performed in a two-electrode undivided completely-mixed and thermostated electrochemical cell of 150 ml capacity. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were rectangular with 2.5 cm^2 geometric area. Linear-sweep voltammograms were determined in the same cell equipped with a third electrode of KCl-saturated Ag/AgCl ($E^\circ = 197 \text{ mV}$ vs SHE at 35 °C) as reference electrode and without stirring.

2.4. Preparation of the diamond electrode (BDD electrode)

Boron-doped diamond (BDD) films were provided by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si $\langle 100 \rangle$ wafers (Siltronix). The reactive gas was methane in excess of dihydrogen. The dopant gas was trimethylboron. Table 1 summarizes the main characteristics of the lots of conductive-diamond electrodes used in this work. These electrodes correspond to different lots sold during the recent years (they were not manufactured exclusively for this study but just provided from Adamant stock). Characterization of conductive-diamond lots were carried out by Adamant Technologies and reported in a particular certificate for every lot. These certificates contained information about boron contents, sp^3/sp^2 ratio, thickness of the diamond layer, roughness of the p-Si substrate and resistivity of the p-Si substrate. Every lot consisted of three sample-electrodes of 2.5 cm^2 .

2.5. Experimental procedures

Lab-scale electrolyses of 100 cm^3 of wastewater were carried out under galvanostatic conditions to determine the influence of the main characteristics of the conductive-diamond layers tested. In all cases a solution composed of $0.44 \text{ mmol dm}^{-3}$ enrofloxacin and 0.05 mol dm^{-3} Na_2SO_4 was utilized. Its pH was adjusted to 3.0 with sulphuric acid and is always kept constant within ± 0.1 units by continuous addition of sodium hydroxide. The current density

Table 1
Characteristics of the conductive-diamond electrodes lots used in this work.

Commercial reference of the BDD	Conductive-diamond layer			p-Si substrate	
	Boron contents (ppm)	Ratio sp^3/sp^2	Thickness BDD layer (μm)	Si-resistivity (mΩ cm)	Roughness, Si-Surfinra (μm)
WD 1049-4	100	65	1.09	100	0.3–0.5
WD 1050-4	200	75	1.14	100	0.3–0.5
LD 60-61-G1	500	93	2.4	100	0.3–0.5
WD 1038-4	1300	66	1.33	100	0.3–0.5
WD 825-6	1300	45	2.33	100	<0.1
WD 908-5	2500	68	1.15	100	<0.1
WD 983-5	1300	77	2.27	10	0.3–0.5
WD 792-1	100	89	1.03	10	<0.1
WD 805-1/3	1300	105	2.25	10	<0.1
WD 858-5	2500	43	1.13	10	<0.1
WD 802-3	8000	80	1.05	10	<0.1

employed was 400 A m^{-2} and the temperature was maintained at 35°C . The cell voltage did not vary during each electrolysis, indicating that conductive-diamond layers did not undergo appreciable deterioration or passivation phenomena.

Linear sweep voltammograms for the oxidation of untreated and treated enrofloxacin solutions at the different conductive-diamond layers were recorded at a scan rate of 500 mV min^{-1} . Before and after each voltammetric experiment, the anode surface was cleaned by electrolyzing 100 ml of a 50 mM Na_2SO_4 solution at 100 mA for 30 min.

3. Results and discussion

Fig. 1 shows the changes in TOC and COD during the electrolyses of an enrofloxacin-polluted synthetic wastewater in a batch mixed electrochemical cell equipped with two different samples of WD 983-5 anode (sp^3/sp^2 ratio of 77 and boron content of 1300 ppm as diamond specifications). It can be observed that both parameters decrease with the current charge passed in a similar way for the three essays made. This seems to indicate that CDEO is a good choice for the removal of this complex pollutant. Thus, taking into account previous studies of our groups [11–22] it can be considered that this technology can be successfully used for the treatment of a great variety of pollutants. If the obtained COD data are compared to the expected for an efficiency of 1 (dashed line in the COD graph of Fig. 1) it seems clear that the efficiency of the process is not high. This can be explained taking into account the small concentration of pollutants in the synthetic raw waste used. Under these conditions, the rate of the process is not controlled by the electrode reaction but by mass transfer. However, this case is the most frequent in the use of CDEO as a treatment technology

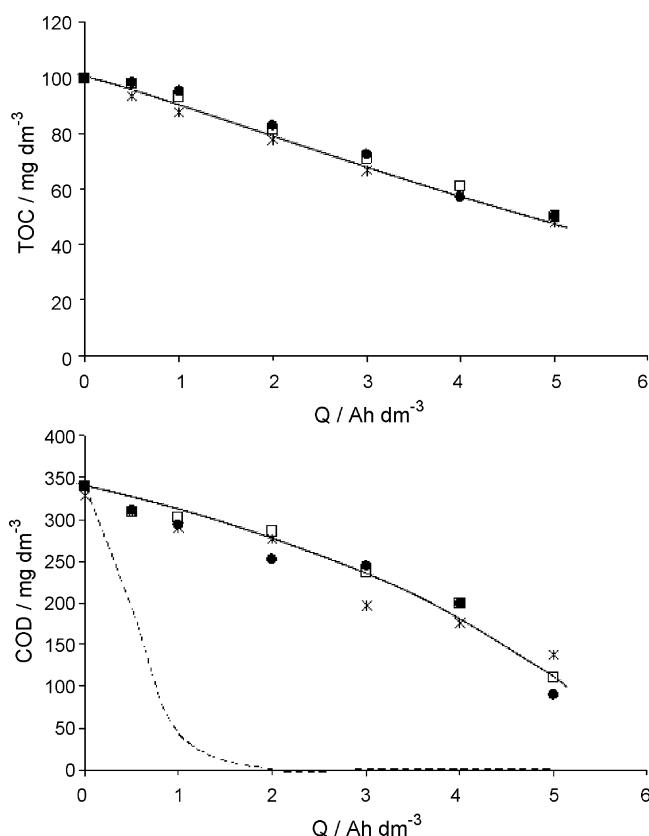


Fig. 1. Changes in TOC and COD during several bulk electrolyses of enrofloxacin ($0.44 \text{ mmol dm}^{-3}$) using a WD 983-5 anode (diamond specifications: sp^3/sp^2 ratio 77 and boron content 1300 ppm). Essays: *, 1, □, 2 and ●, 3.

and in this work it has been preferred to maintain these typical conditions for the whole study.

Another important observation is the significant decrease in TOC from the very first stages of the process. This suggests that the electrochemical oxidation of enrofloxacin leads finally to carbon dioxide. However, the percentage of COD removed after consumption of 5 Ah dm^{-3} (67.4%) is higher than the percentage of TOC removed (51.0%) and this clearly indicates the formation of intermediates during the electrolysis and hence its mineralization (transformation of enrofloxacin into carbon dioxide) does not behave as a direct mineralization process. This means that once the molecule is adsorbed onto the diamond, its oxidation intermediates do not remain on its surface up to the complete transformation into CO_2 , but they are desorbed and accumulated in the medium.

The dispersion in the measurement of TOC in Fig. 1 is smaller than that found for COD. This can be explained by the higher accuracy in the determination of the former parameter. Anyway, the reproducibility of results is rather good, especially if we take into account that the two first essays were carried out with the same WD 983-5 electrode and the third one with another electrode of equal characteristics.

As the goal of the paper is the comparison of diamond electrodes, reproducibility is a key factor. For this reason, to check the good reproducibility of the electrolyses, several tests were carried out with different types of diamond electrodes. Fig. 2 summarises the results of this reproducibility study. It can be observed that the use of different types of diamond results in different TOC and COD removals after the same charge passed during the electrolyses. Conversely, the use of the same type of diamond leads to similar results. It can also be corroborated that TOC data are more accurate, as it was previously explained in terms of the bad reproducibility of

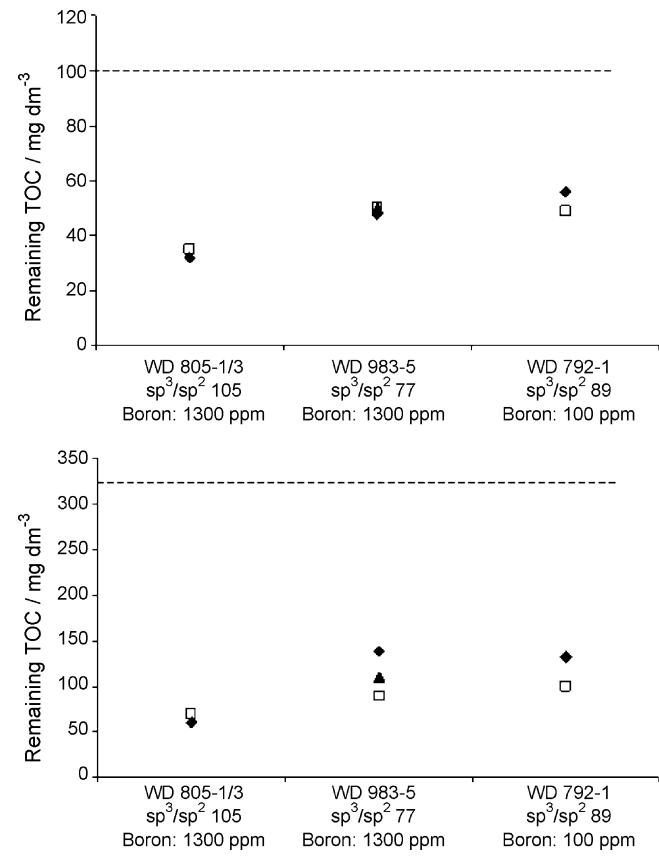


Fig. 2. Reproducibility tests. Remaining concentration of TOC and COD after electrolyses of enrofloxacin ($0.44 \text{ mmol dm}^{-3}$) with three different types of diamond (specific current charge passed of 5 Ah dm^{-3}).

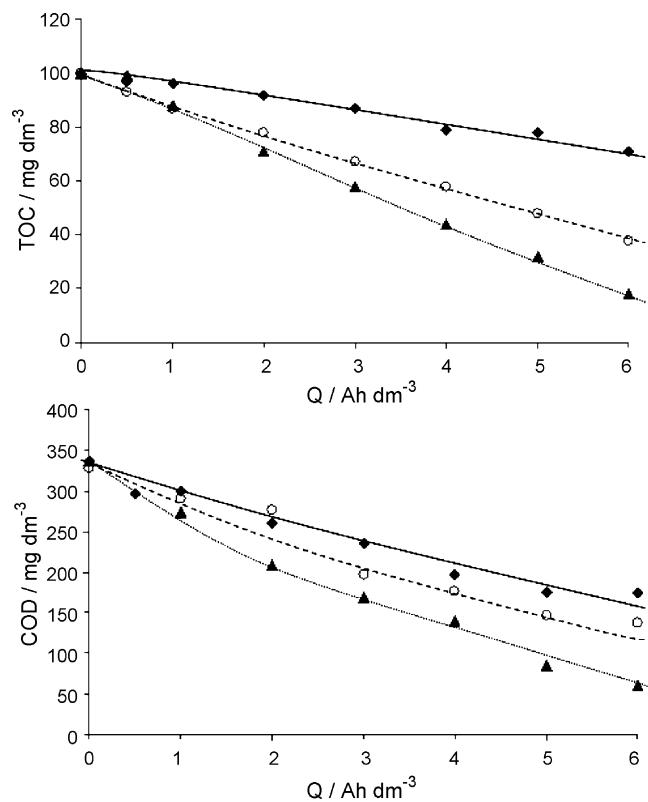


Fig. 3. Effect of the sp^3/sp^2 ratio of the boron-doped diamond anode on the TOC and COD abatements during bulk electrolyses of enrofloxacin solutions ($0.44\ mmol\ dm^{-3}$). sp^3/sp^2 ratio: \blacklozenge , 45 (WD 825-6), \circ , 77 (WD 983-5), \blacktriangle , 105 (WD 805-1/3).

COD measurements. However, the use of both parameters (TOC and COD) in this study is important, because both parameters give different information: a decrease in the COD indicates oxidation (change in the chemical species) while a decrease in the TOC is related to mineralization (conversion into carbon dioxide).

Fig. 3 shows the effect of the diamond to graphite ratio in the performance of the electrolyses. For the three studied ratios, CDEO is able to oxidize enrofloxacin. However, as it can be seen, the higher the content in diamond the greater the TOC and COD decays in the bulk electrolyses. Differences between the results obtained in the electrolyses with the different diamonds are higher in terms of the TOC changes than in COD changes. This can be clearly observed in Fig. 4 where the percentage of TOC and COD removal are compared after a current charge passed of $6\ Ah\ dm^{-3}$.

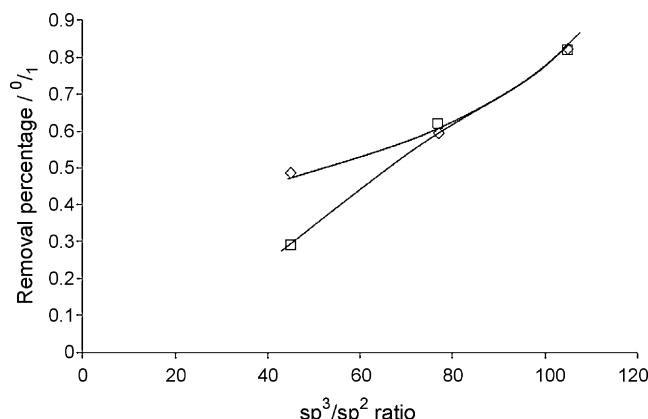


Fig. 4. Influence of the diamond to graphite carbon on the percentage of (□) COD and (\diamond) TOC removal after a current charge passed of $6\ Ah\ dm^{-3}$.

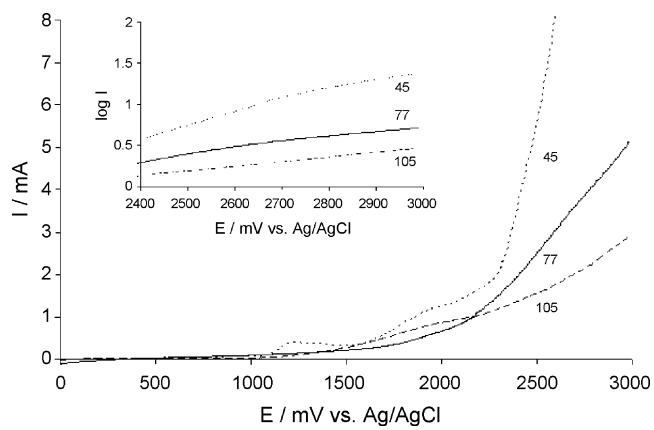


Fig. 5. Effect of the sp^3/sp^2 ratio (given in each curve) on the linear-sweep voltammograms of the oxidation of enrofloxacin solutions ($0.44\ mmol\ dm^{-3}$). Inset: Tafel slopes in the supporting electrolyte instability zone.

The diamond with the high graphite content leads to the formation of many intermediates (the change in COD is almost the double of the change in TOC) while in the diamonds with a higher content of sp^3 carbon the percentages are quite similar and the only way to explain this observation, it is assuming that all organics that became oxidized are completely converted into CO_2 . This suggests that the oxidation carried out by the diamond with the lower content of sp^3 -carbon is softer.

Fig. 5 shows the voltammetric behaviour of the enrofloxacin solution at these three electrodes before the bulk electrolyses. It can be observed an increase in the direct electrochemical activity with increasing the graphite content. For the highest content of graphite, one little anodic oxidation peak is clearly exhibited at $1300\ mV$ vs $Ag/AgCl$ which has to be related to the direct oxidation of enrofloxacin. In addition, a small shoulder appears around $2000\ mV$ vs $Ag/AgCl$. According to previous studies [32], this shoulder can be related to the oxidation of sulphates contained in the waste as electrolyte. Conversely, the other two electrodes with higher diamond content only displayed the shoulder, but not any anodic peak. This means that direct oxidation of enrofloxacin is not promoted with these electrodes. Another important fact is that the Tafel slopes in the region of instability of the supporting electrolyte (inset of Fig. 5) remain almost the same with the diamond to graphite ratio. In fact, the differences observed in the voltammogram are due not to oxygen evolution but to a previous process. From these results, it is apparent that higher content of graphite in the diamond electrode leads to a higher direct electrochemical activity and to a lower bulk electrolyses efficiency. The higher electrochemical activity is probably related to the better adsorption of reactants on sp^2 carbon. On the contrary, the better results obtained in the bulk electrolyses by higher content in diamond-carbon should be caused by the oxidants generated in the supporting electrolyte region that are promoted when the electrochemical activity towards enrofloxacin is smaller.

Fig. 6 presents the effect of the boron content of the diamond electrode on the performance of the electrolyses. The changes are not as sharp as those observed in the case of the sp^3/sp^2 ratio, but it appears that the process is improved with increasing the concentration of boron on the diamond surface. An inhibition in TOC decay up to values approximately $2\ Ah\ dm^{-3}$ with raising the boron content can be observed, whereupon the opposite trend occurs and the mineralization is enhanced as the diamond becomes richer in boron. This means that during the first oxidation stage the formation of carbon dioxide is not promoted in the electrolyses with highly doped boron anodes in spite of the higher

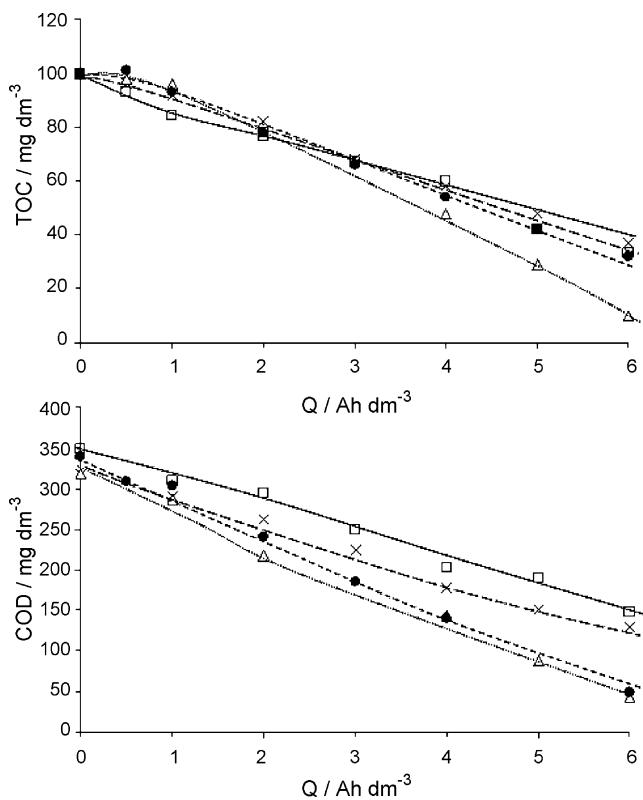


Fig. 6. Effect of the boron content of the diamond anode on the removal of TOC and COD during bulk electrolyses of enrofloxacin solutions ($0.44 \text{ mmol dm}^{-3}$). Boron content: \square , 100 mg dm^{-3} (WD 1049-4); \times , 200 mg dm^{-3} (WD 1050-4); \bullet , 1300 mg dm^{-3} (WD 1038-4); \triangle , 2500 mg dm^{-3} (WD 908-5).

COD removal that achieves during the complete treatment. This suggests the formation of intermediates during this first stage that consume the oxidants without complete mineralization.

Fig. 7 shows the linear-sweep voltammeteries carried out before bulk electrolyses using diamonds with different boron content. In this case, it is interesting to remark that the anodic oxidation peak at ca. 1300 mV vs Ag/AgCl related to the direct electrochemical oxidation of enrofloxacin only appears for the diamond containing 2500 ppm of boron, which seems to be less important and masked with starting oxygen evolution for the other electrodes with much smaller dopant. It is also noticeable the little influence of the boron content on the Tafel slopes in the supporting electrolyte instability region (inset of Fig. 7).

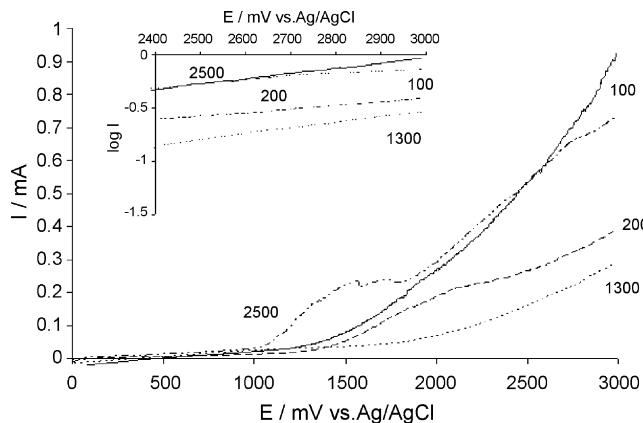


Fig. 7. Effect of the boron content of the diamond anode (given in each curve as ppm) on the linear-sweep voltammograms of the oxidation of enrofloxacin solutions ($0.44 \text{ mmol dm}^{-3}$). Inset: Tafel slopes in the supporting electrolyte instability zone.

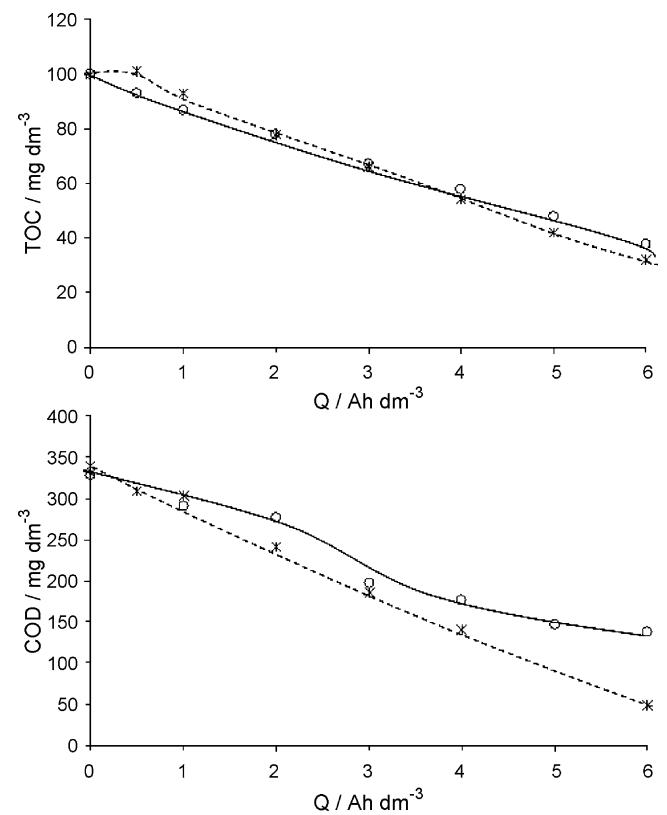


Fig. 8. Effect of the thickness of the BDD layer on TOC and COD decays during bulk electrolyses of enrofloxacin solutions ($0.44 \text{ mmol dm}^{-3}$). Thickness of the BDD layer: \circ , $2.27 \mu\text{m}$ (WD 983-5); \times , $1.33 \mu\text{m}$ (WD 1038-4).

Fig. 8 shows the effect of the thickness of the diamond layer on TOC and COD decays. The thinner the layer, the higher the oxidation rate. This result was also previously found in the oxidation of phosphates to perphosphates [23] and in this case it was explained in terms of the migration of silicon atoms from the support to the surface of the diamond electrode, thus favouring oxidation processes. The generation of higher concentrations of oxidants than later can help to the oxidation of enrofloxacin and intermediates can then explain the better performance obtained at greater layer thickness. The main differences in the voltammetric study carried out in this work were found for this parameter.

Fig. 9 compares the voltammetric behavior for enrofloxacin oxidation using two electrodes of 1.33 and $2.27 \mu\text{m}$ thickness. It

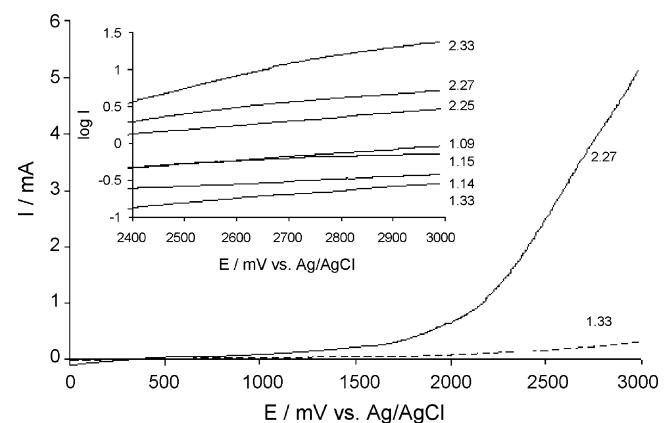


Fig. 9. Effect of the diamond layer thickness (given in each curve as μm) on the linear-sweep voltammograms of enrofloxacin solutions ($0.44 \text{ mmol dm}^{-3}$). Inset: Tafel slopes in the supporting electrolyte instability zone for different electrodes.

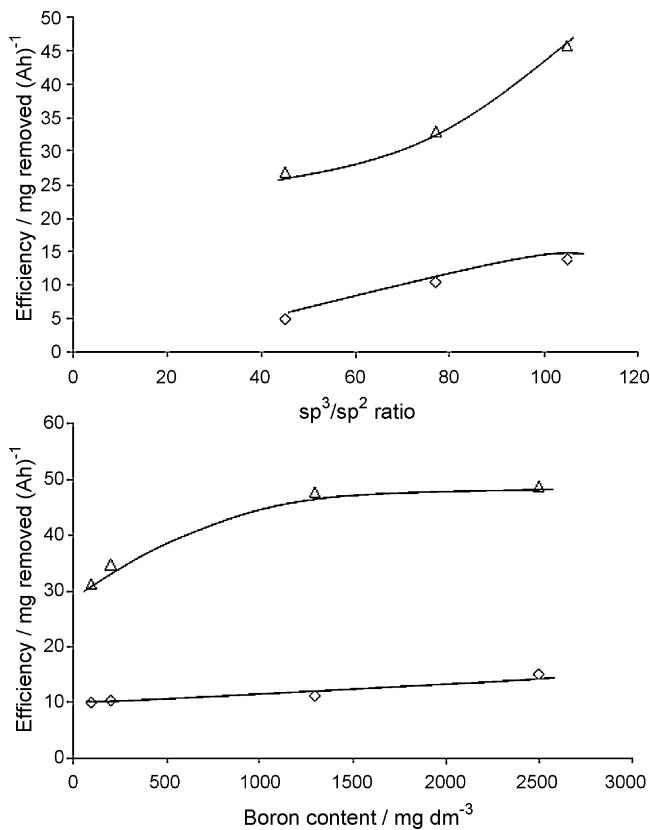


Fig. 10. Changes in the average efficiency of (△) COD and (◇) TOC removal with the sp^3/sp^2 ratio and boron content during bulk electrolyses of enrofloxacin solutions ($0.44 \text{ mmol dm}^{-3}$).

seems clear that the direct electrochemical activity is promoted in the electrode with the thicker diamond layer. This is also observed on the onset in which the logarithmic plot for the region of instability of supporting electrolytes are shown for all the electrodes used in this work. The apparent exchange current density seems to be greatly influenced by the thickness but the Tafel slope seems to be almost the same in all cases. This confirms that electrodes that are more electrocatalytic towards direct oxidation of enrofloxacin give worse results in bulk electrolyses and hence, the less electrocatalytic thinner diamonds will be preferable for a faster electrolytic degradation, as shown in Fig. 8.

Finally, Fig. 10 compares the average efficiency of the treatments in terms of COD and TOC with the sp^3/sp^2 ratio and boron content. With regard to the treatment results for the efficiency in the oxidation of COD, the higher the content in sp^3 carbon and in boron the better the efficiency in the COD removal. The influence on the mineralization (efficiency in TOC removal) of the sp^3 content is also important but much less relevant than the boron content.

4. Conclusions

Properties of the diamond layer strongly influences on the results of the electrochemical oxidation of enrofloxacin. Particularly, the ratio diamond/graphite carbon was found one of the most significant parameter in this process: the higher the content in diamond-carbon the greater the TOC and COD decays in the bulk

electrolyses. This may be explained by the formation of intermediates. High graphite content leads to the formation of many intermediates while high diamond content seems to favour the complete oxidation of the organic to carbon dioxide. Likewise, the oxidation rate seems to be improved with increasing the concentration of boron and decreasing the thickness of the substrate layer.

Acknowledgements

The financial support of Spanish government through projects CONSOLIDER-INGENIO 2010 (CSD2006-0044) and CTQ2007-60708/BQU, cofinanced with FEDER funds, is gratefully acknowledged. This work was also supported by the JCCM (Junta de Comunidades de Castilla La Mancha, Spain) through the Projects PBI-06-013 and PCI-08-0068-9073. Authors also thank ADAMANT TECHNOLOGIES for providing the lots of electrodes used in this work.

References

- [1] S. Castiglioni, R. Bagnati, R. Fanelli, F. Pomati, D. Calamari, E. Zuccato, Environ. Sci. Technol. 40 (2006) 357–363.
- [2] K.G. Karthikeyan, M.T. Meyer, Sci. Total Environ. 361 (2006) 196–207.
- [3] R.H. Lindberg, U. Olofsson, R. Per, M.I. Johansson, M. Tysklind, B.A.V. Andersson, Environ. Sci. Technol. 40 (2006) 1042–1048.
- [4] N. Vieno, T. Tuukkanen, L. Kronberg, Water Res. 41 (2007) 1001–1012.
- [5] W. Xu, G. Zhang, S. Zou, X. Li, Y. Liu, Environ. Pollut. 145 (2007) 672–679.
- [6] M. Seifertova, A. Pena, C.M. Lino, P. Solich, Anal. Bioanal. Chem. 391 (2008) 799–805.
- [7] F. Tamtam, F. Mercier, B. Le Bot, J. Eurin, Q.T. Dinh, M. Clement, M. Chevreuil, Sci. Total Environ. 393 (2008) 84–95.
- [8] R. Andreozzi, M. Raffaele, P. Nicklas, Chemosphere 50 (2003) 1319–1330.
- [9] E. Brillas, I. Sirés, C. Arias, P.L. Cabot, F. Centellas, R.M. Rodríguez, J.A. Garrido, Chemosphere 58 (2005) 399–406.
- [10] A.J. Watkinson, E.J. Murby, S.D. Costanzo, Water Res. 41 (2007) 4164–4176.
- [11] E. Guinea, C. Arias, P.L. Cabot, J.A. Garrido, R.M. Rodríguez, F. Centellas, E. Brillas, Water Res. 42 (2008) 499–511.
- [12] E. Brillas, B. Boye, I. Sirés, J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot, Ch. Comninellis, Electrochim. Acta 49 (2004) 4487–4496.
- [13] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Water Res. 39 (2005) 2687–2705.
- [14] P. Cañizares, R. Paz, C. Sáez, M.A. Rodrigo, J. Electrochim. Soc. 154 (2007) E165–E171.
- [15] P. Cañizares, R. Paz, C. Sáez, M.A. Rodrigo, Electrochim. Acta 53 (2008) 2144–2153.
- [16] M. Faouzi, P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M.A. Rodrigo, C. Sáez, Electrochim. Acta 52 (2006) 325–331.
- [17] M. Panizza, A. Barbucci, R. Ricotti, G. Cerisola, Sep. Purif. Technol. 54 (2007) 382–387.
- [18] M. Panizza, A. Kapalka, Ch. Comninellis, Electrochim. Acta 53 (2008) 2289–2295.
- [19] A.M. Polcaro, M. Mascia, S. Palmas, A. Vacca, Electrochim. Acta 49 (2004) 649–656.
- [20] A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, Electrochim. Acta 50 (2005) 1841–1847.
- [21] I. Sirés, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, E. Brillas, Electrochim. Acta 52 (2006) 75–85.
- [22] M. Skoumal, C. Arias, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, E. Brillas, Chemosphere 71 (2008) 1718–1729.
- [23] P. Cañizares, C. Sáez, F. Martínez, M.A. Rodrigo, Electrochim. Solid-State Lett. 11 (2008) E15–E19.
- [24] P. Cañizares, C. Sáez, A. Sánchez-Carretero, M.A. Rodrigo, Electrochim. Commun. 10 (2008) 602–606.
- [25] M. Gattrell, D.W. Kirk, J. Electrochim. Soc. 140 (1993) 903–911.
- [26] M. Gattrell, D.W. Kirk, J. Electrochim. Soc. 140 (1993) 1534–1540.
- [27] N. Belhadj Tahar, A. Savall, J. Electrochim. Soc. 145 (1998) 3427–3434.
- [28] I. Duo, A. Fujishima, Ch. Comninellis, Electrochim. Commun. 5 (2003) 695–700.
- [29] I. Duo, C. Levy-Clement, A. Fujishima, C. Comninellis, J. Appl. Electrochim. 34 (2004) 935–943.
- [30] M. Panizza, P.A. Michaud, G. Cerisola, Ch. Comninellis, J. Electroanal. Chem. 507 (2001) 206–214.
- [31] E.M. Golet, I. Xifra, H. Siegrist, A.C. Alder, W. Giger, Environ. Sci. Technol. 37 (2003) 3243–3249.
- [32] P. Cañizares, C. Sáez, R. Paz, J. Lobato, M.A. Rodrigo, J. Electrochim. Soc. 154 (2007) E37–E44.